METAL-ASSISTED SYNTHESES OF BORANES AND CARBORANES

Final Report

Russell N. Grimes

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FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Methods were developed for (i) the systematic preparation of organosubstituted derivatives of small carboranes, especially of the type *nido*-$RR'C_2B_4H_6$ where R and R' are alkyl, aryl, or arylalkyl groups; (ii) oxidative fusion of these compounds to large $R_2R'_2C_4B_8H_8$ clusters via transition metal-promoted fusion; (iii) conversion of the nido-carboranes to stable (arene)metal(carborane) complexes incorporating first-, second-, or third-row transition series metals; (iv) stacking of the metal-carborane complexes to produce novel triple- and multi-decker sandwich complexes containing two or more metal centers; (v) synthesis of B-substituted carboranes and metallacarboranes via controlled regiospecific pathways; and (vi) studies of the chemical reactivity of the nido-carboranes and their derived metal complexes. The nonmetallated new carboranes are potentially useful in VHBR (very high burning rate) applications, while the metal sandwich complexes are precursors to high molecular weight polymers or solid state materials having novel electronic properties.

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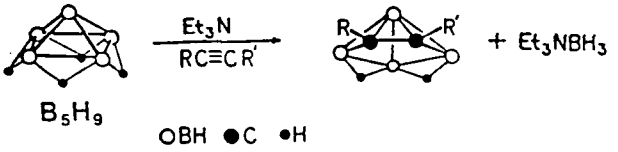
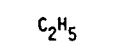
I. Statement of Problem

This research was concerned with the development of rational, efficient syntheses of small nido-carboranes, their metal-promoted conversion to larger clusters, and their incorporation into stable organometallic complexes including structurally novel triple- and multi-decker transition-metal sandwich complexes.

II. Summary of Important Results

1. Designed synthesis of nido-$RR'C_2B_4H_6$ "building-block" carborane reagents. The method developed originally in this laboratory, involving attack of $RC{\equiv}CR'$ alkynes on B_5H_9, was extended to generate a large variety of C-substituted carborane derivatives including bis-, tris-, and cyclic carboranes as shown. These materials were prepared as potential candidates for VHBR testing and also as ligands for the construction of tailored metal sandwich complexes, described below.



R	R′
CH_3	CH_3
C_2H_5	C_2H_5
$n\text{-}C_3H_7$	$n\text{-}C_3H_7$
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$
$i\text{-}C_5H_{11}$	$i\text{-}C_5H_{11}$
$n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}$
$n\text{-}C_4H_9$	
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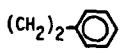
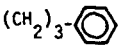
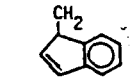
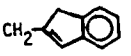
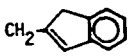
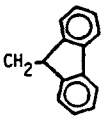
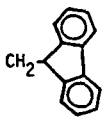
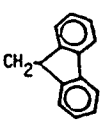
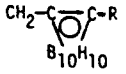
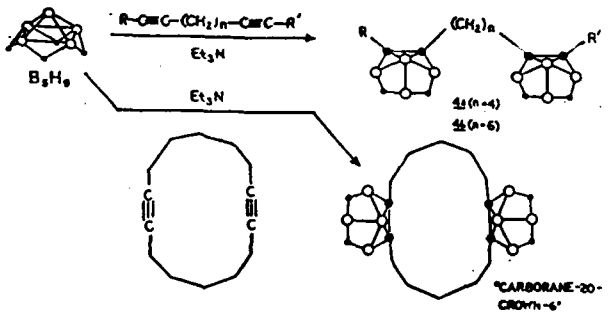
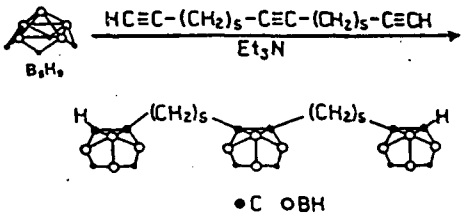
✱ 	
	
	H

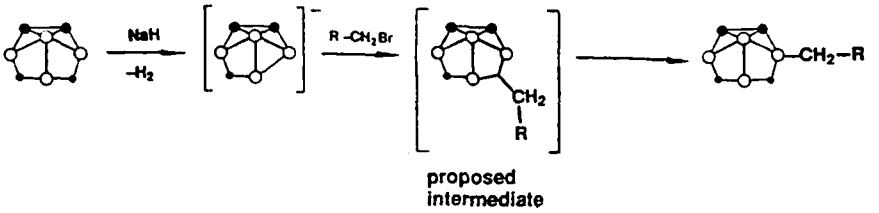
R	R′
	H
	H
	
	H
	
	H

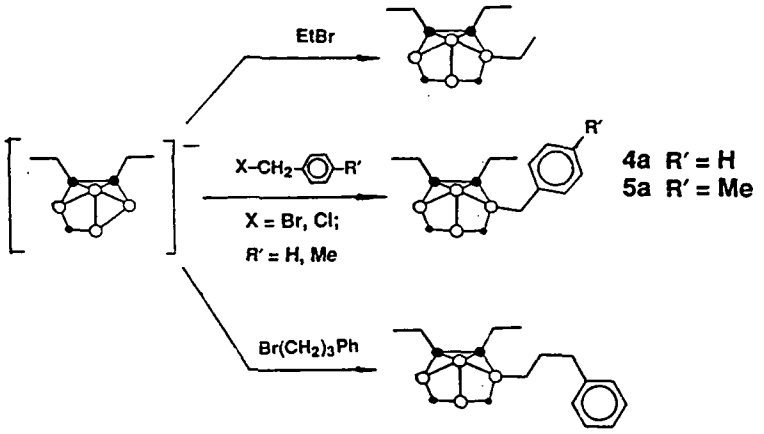
✱ Obtained at 180° in absence of Et_3N.

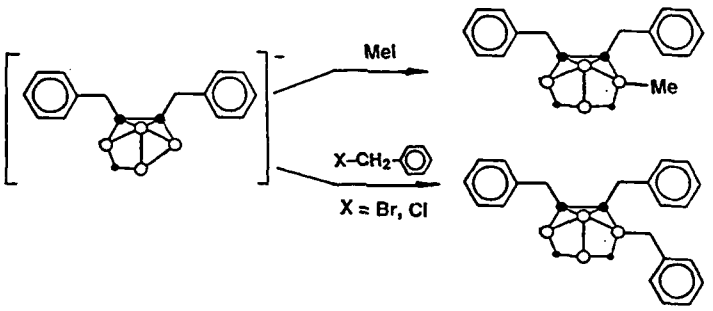




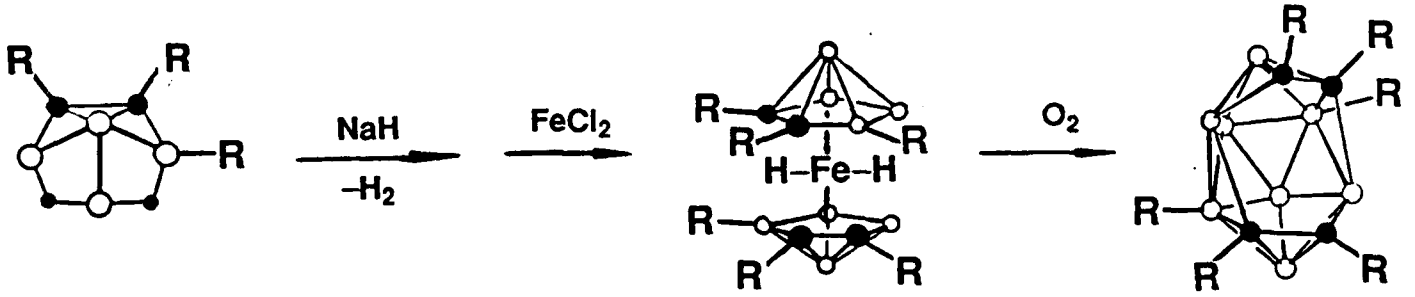
2. Controlled substitution at boron in $R_2C_2B_4H_6$ compounds. A regiospecific synthesis of B(2/4)-monosubstituted derivatives was developed as shown, thereby enlarging still further the range of nido-carborane species available as building-block reagents (previously restricted to C-substituted derivatives as in part 1 above).





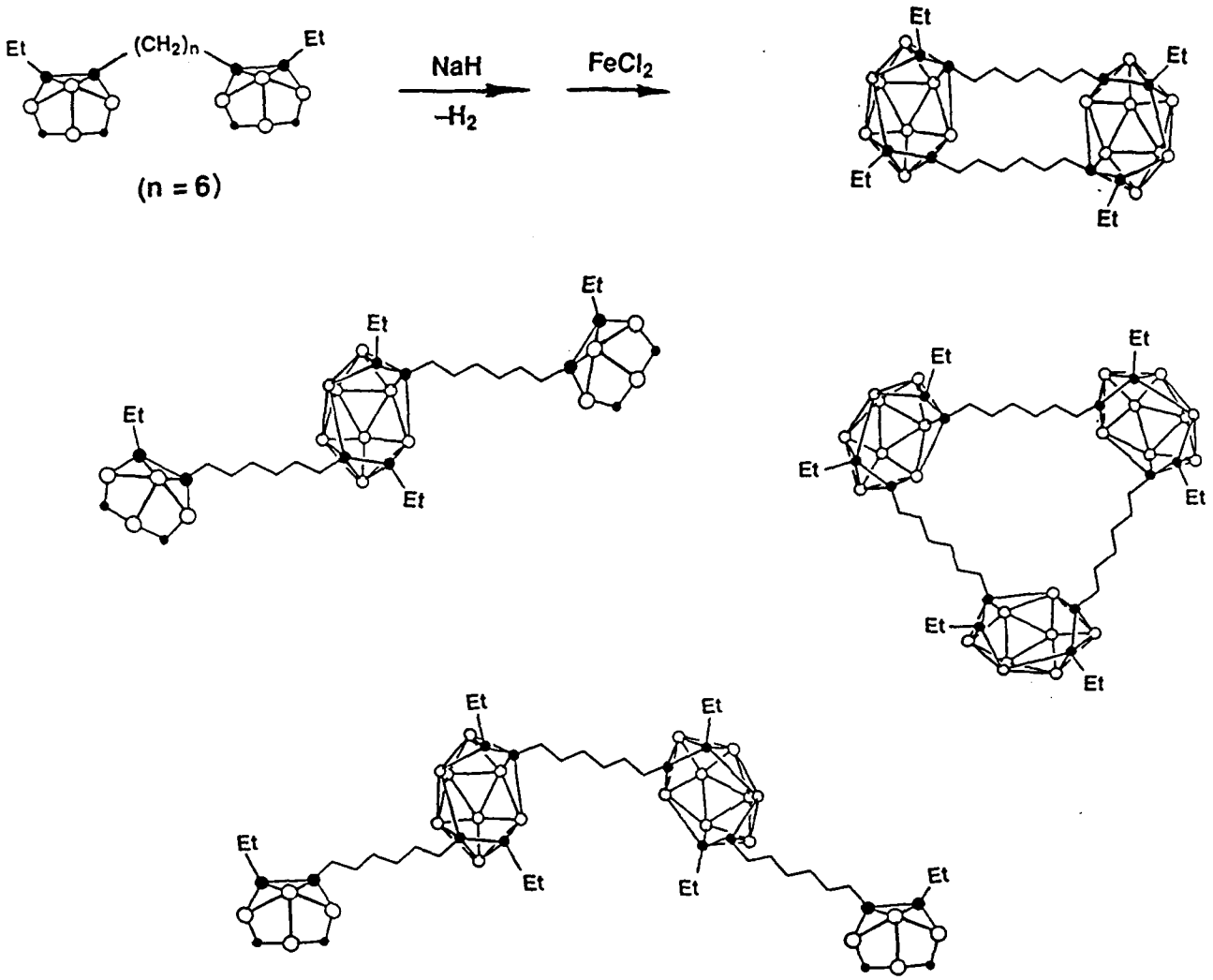


3. Metal-promoted fusion of polysubstituted and bulky-substituted nido-carboranes. Our previous studies of fusion of C_2B_4 carboranes via metal complex intermediates of the type $(R_2C_2B_4H_4)_2FeH_2$ were extended to the boron-substituted species, with the finding that fusion does occur giving the corresponding hexasubstituted C_4B_8 clusters:

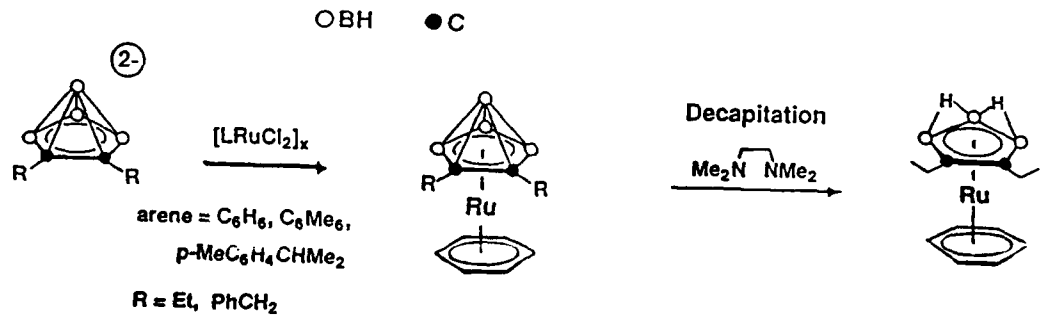


R = Et, CH_2Ph

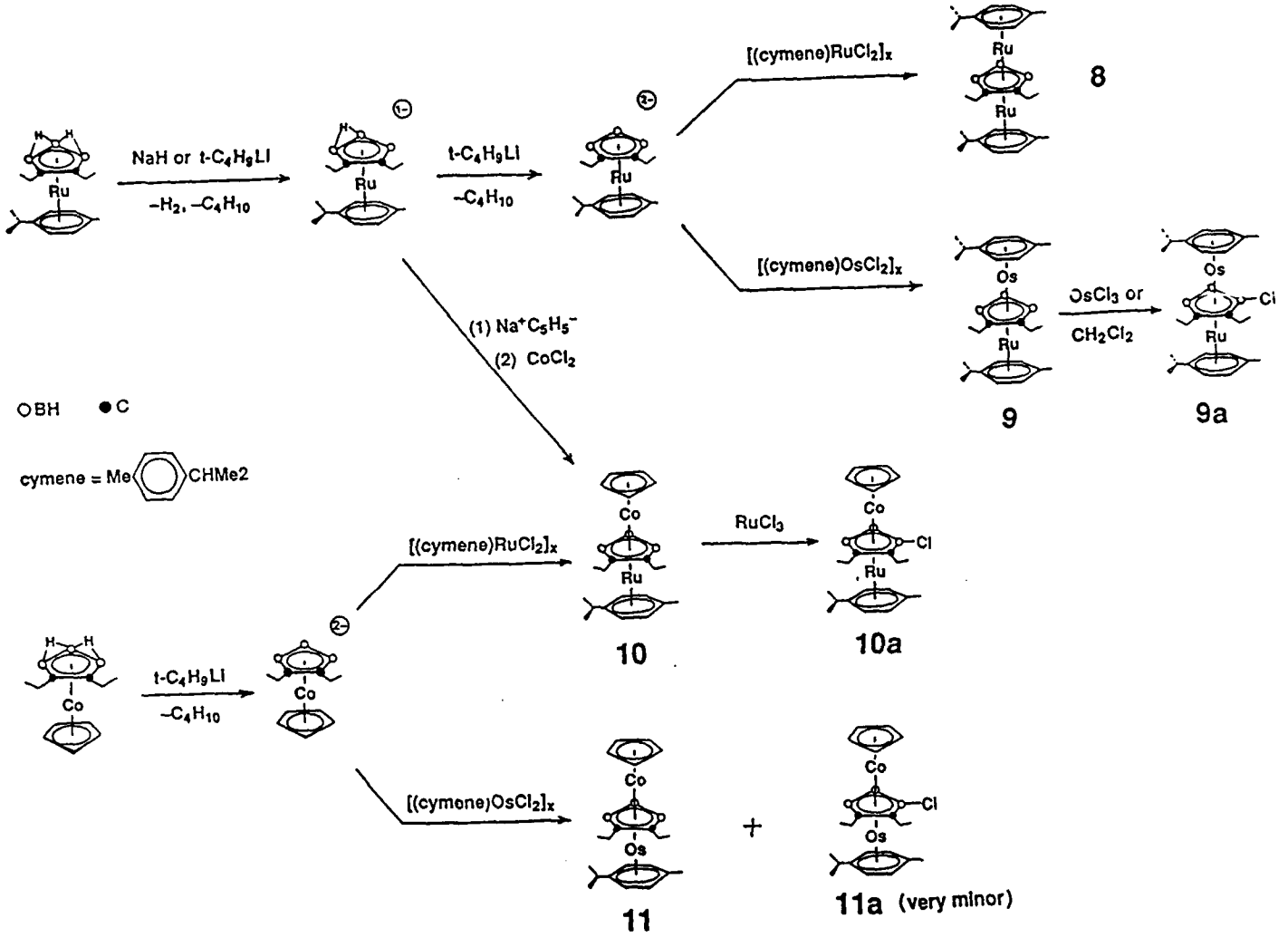
Fusion was also found to occur even with the bis- and triscarboranes described above, and with mono- and bis(chromium tricarbonyl) complexes of $Ph_2C_2B_4H_6$:



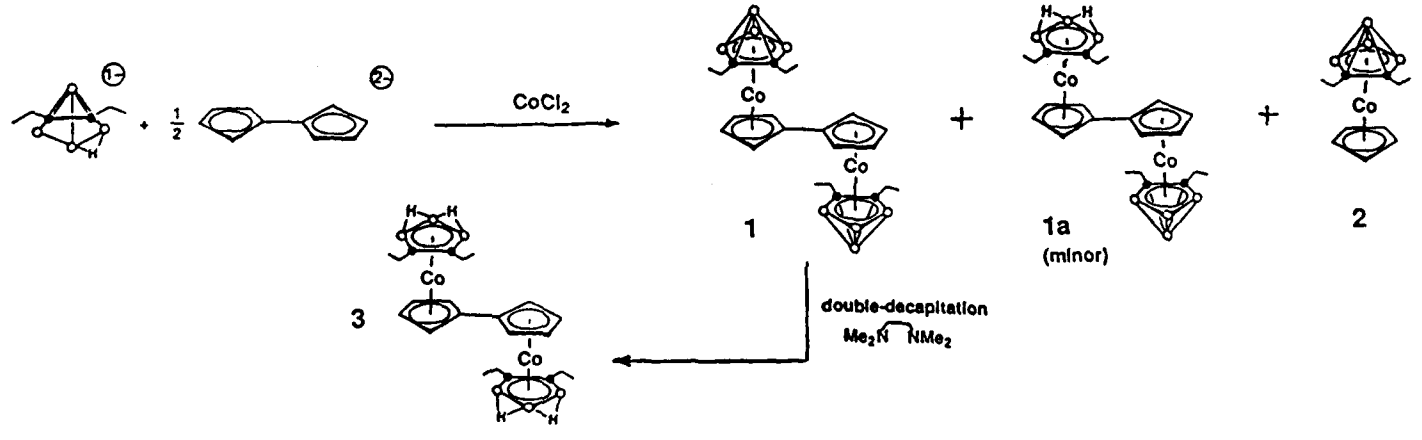
4. Designed synthesis of $(C_2B_4)M(arene)$ and $(C_2B_3)M(arene)$ sandwich complexes. Controlled routes to crystalline, air-stable species containing cobalt, ruthenium, osmium, or iron were developed. "Decapitation" (base-induced removal of the apex BH unit) of the C_2B_4 complexes generates the corresponding *nido*-C_2B_3 species, which can accept addition metal-ligand units to generate triple-deckers (see following section).

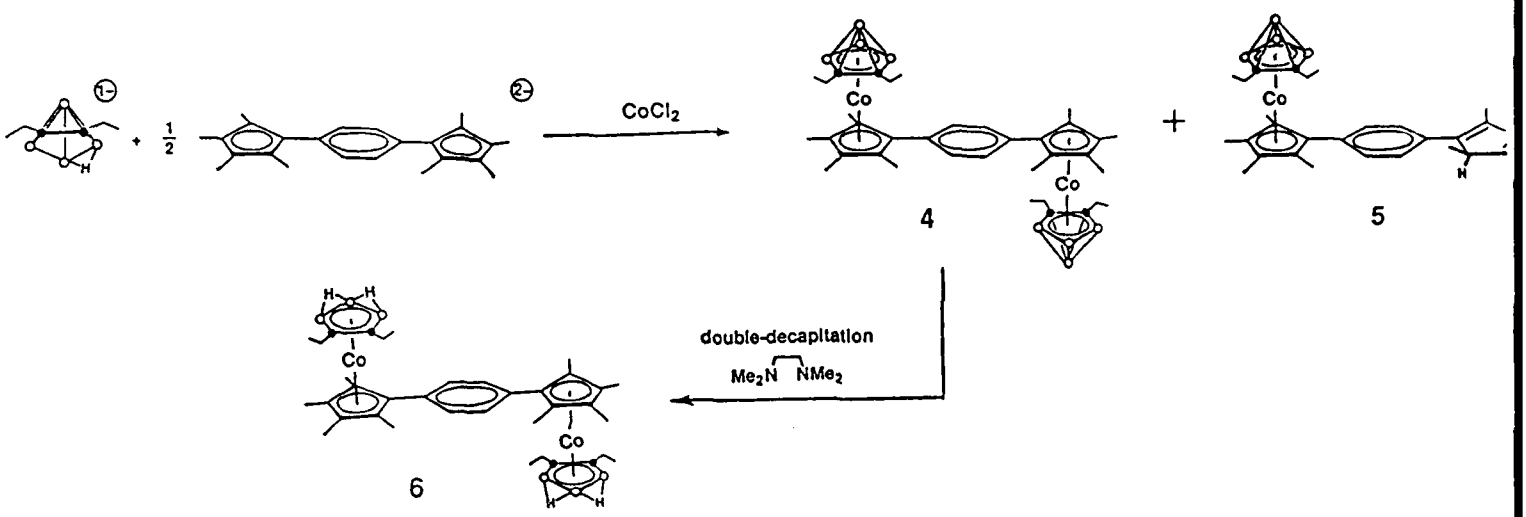


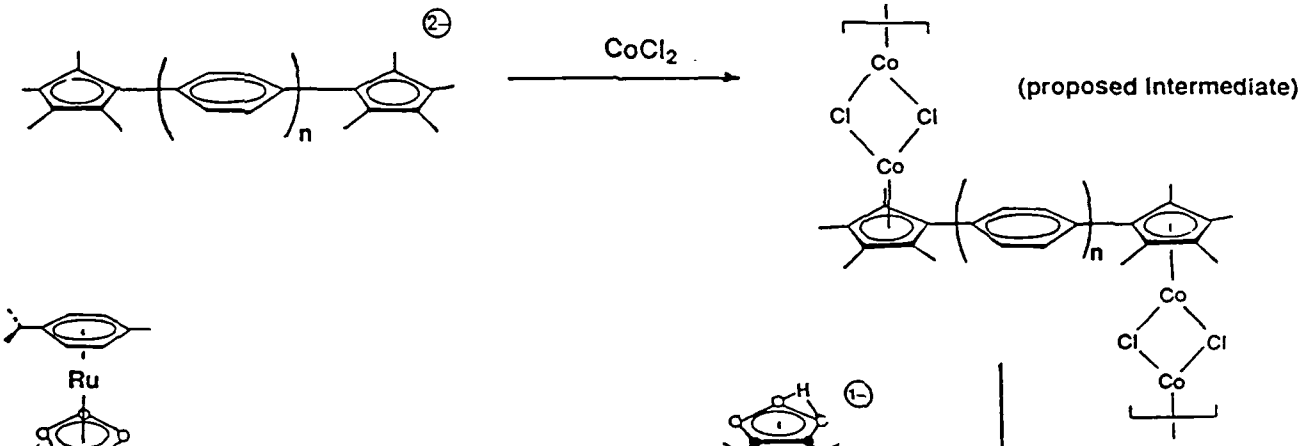
*5. **Designed synthesis of triple-decker complexes.*** Routes were found to homo- and heterobinuclear triple-decker sandwiches containing bridging C_2B_3 cyclo-carborane rings, including the first such species incorporating second- or third row transition metals. Species **8** and **10** were crystallographically characterized.

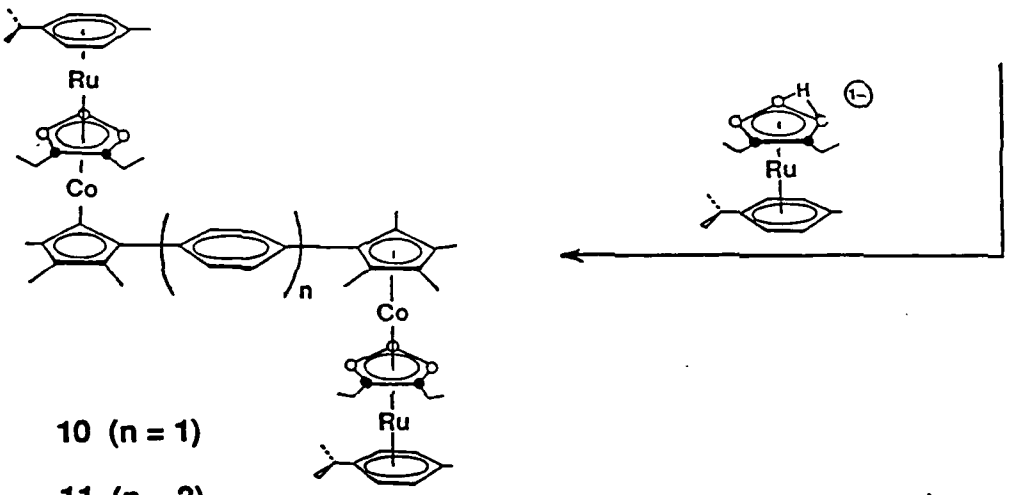


*6. **Designed synthesis of linked multiunit double- and triple-decker sandwich complexes.*** As a stepping-stone to electron-delocalized polymers, novel fulvalene-based and phenylene-linked species were prepared as shown. Structural characterization by X-ray crystallography were obtained for compounds **1**, **6**, and **10**.



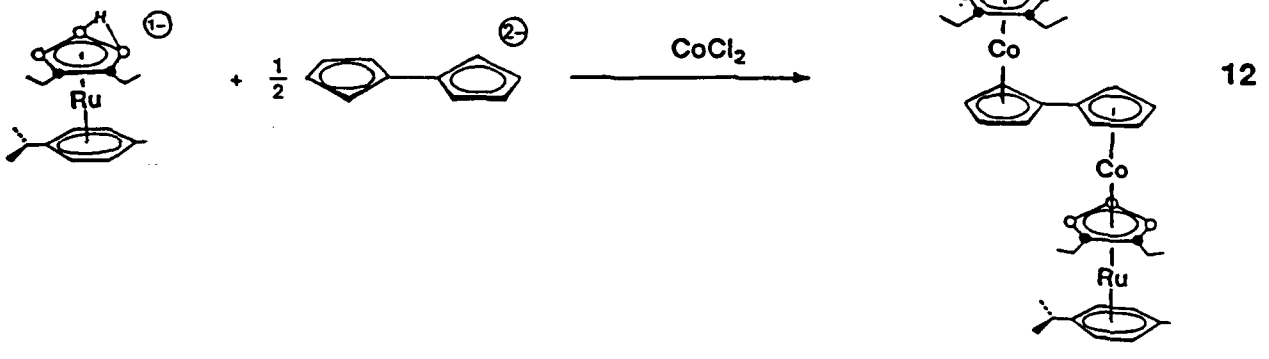

CoCl2
4
5
double-decapitation
Me2N NMe2
6


CoCl2
(proposed Intermediate)



10 (n = 1)

11 (n = 2)



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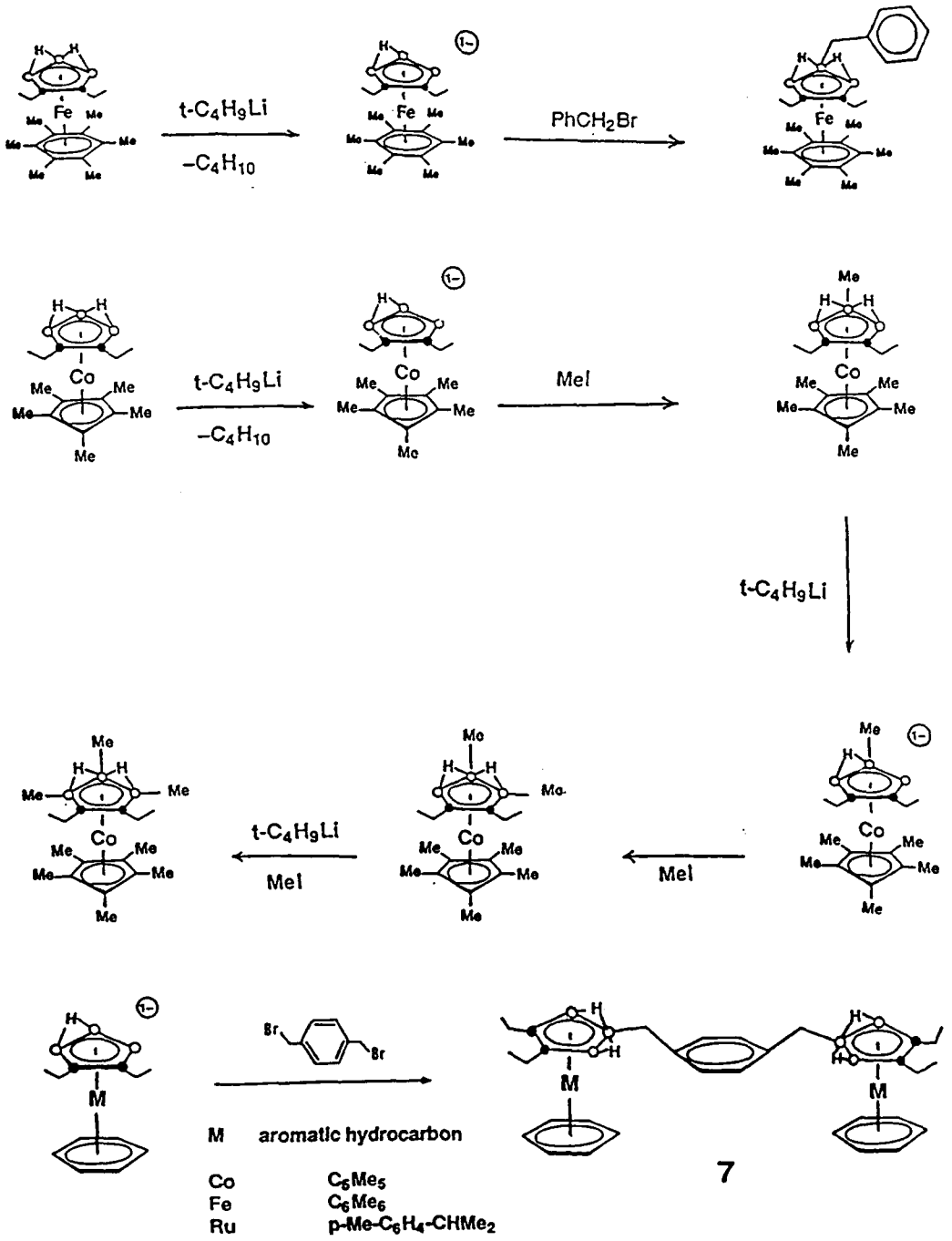
7. Controlled substitution at boron positions in metal-carborane sandwich complexes and construction of B-X-B linked poly(arene-metal-carborane) systems. It was found that the attack of alkyl halides on (arene)M($R_2C_2B_3H_4$)$^-$ anions proceeds in a manner opposite that of the analogous $R_2C_2B_4H_5^-$ carborane ions, giving exclusively B(5)-substituted products, as shown. This finding was exploited in synthesis to generate novel linked multiunit sandwich complexes as illustrated.



7

III. Publications produced under this Contract

J. T. Spencer and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 8. Mono-, Di-, and Triiron Polyarene Sandwich Complexes of $Et_2C_2B_4H_4^{2-}$ Containing Fluorene, 9,10-Dihydroanthracene or [2.2]Paracyclophane Ligands", Organometallics 1987, 6, 323.

J. T. Spencer and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 9. Nido-2,3-Dibenzyl-2,3-dicarbahexaborane(8) [$(PhCH_2)_2C_2B_4H_6$], a Versatile Multifunctional Nido-Carborane: Iron-Polyarene Sandwich Compounds and Chromium Tricarbonyl π-Complexes", Organometallics 1987, 6, 328.

J. T. Spencer, M. R. Pourian, R. J. Butcher, E. Sinn, and R. N. Grimes, Organotransition-Metal Metallacarboranes. 10. π-Complexation of nido-$(PhCH_2)_2C_2B_4H_6$ at the C_2B_3 and C_6 Rings. Synthesis and Crystal Structures of Nido-2,3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5)CH_2]_2$-2,3-$C_2B_4H_6$ and $(PhCH_2)_4C_4B_8H_8$, a Nonfluxional C_4B_8 Cluster", Organometallics 1987, 6, 335.

T. Whelan, J. T. Spencer, M. R. Pourian, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 11. Chromium Tricarbonyl η^6-Complexes of Nido-2,3-$(PhCH_2)_2C_2B_4H_6$: Metal Complexation and Oxidative Fusion", Inorg. Chem. 1987, 26, 3116.

R. N. Grimes, "Synthetic Strategies in Boron Cage Chemistry", in Advances in Boron and the Boranes, Liebman, J. F.; Greenberg, A.; Williams, R. E., Eds.; VCH Publishers, Inc.: New York, 1988, Chapter 11, pp. 235-263.

R. N. Grimes, "Designed Synthesis of Multi-functional Carboranes and Organotransition Metal-Carborane Complexes", Pure and Applied Chem. 1987, 59, 847.

H. A. Boyter, Jr. and R. N. Grimes, "Nido-Carborane Building-Block Reagents. 2. Bulky-Substituent $(Alkyl)_2C_2B_4H_6$ Derivatives and $(C_6H_5)_2C_2B_4H_6$: Synthesis and Properties", Inorg. Chem., 1988, 27, 3075.

H. A. Boyter, Jr. and R. N. Grimes, "Nido-Carborane Building-Block Reagents. 3. Cyclic and Open-Chain Oligomers Incorporating $-CB_4H_6C-$ Units. Crown Carboranes", Inorg. Chem., 1988, 27, 3080.

J. H. Davis, Jr. and R. N. Grimes, "Nido-Carborane Building-Block Reagents. 4. Regiospecific Substitution at Boron in 2,3-$R_2C_2B_4H_6$ Cages. Evidence for Intramolecular C-H---H_{bridge} Interactions in 2,3-$R_2C_2B_4H_5$-4-R' Derivatives", Inorg. Chem., 1988, 27, 4213.

J. H. Davis, Jr., E. Sinn, and R. N. Grimes, "Arene-Metal-Carborane Triple-Decker Sandwiches: Designed Synthesis of Homo- and Heterobimetallic Complexes of Cobalt, Iron, Ruthenium, and Osmium", J. Am. Chem. Soc. 1989, 111, 4776.

J. H. Davis, Jr., E. Sinn, and R. N. Grimes, "Fulvalene- and Polyarene-Transition Metal-Carborane Complexes as Building Blocks for Multilevel Arrays. Stepwise Synthesis of Polymetallic Linked Sandwiches", J. Am. Chem. Soc., 1989, 111, 4784.

J. M. Merkert, W. E. Geiger, J. H. Davis, Jr., M. D. Attwood, and R. N. Grimes, "Carborane-Stabilized M(III) Complexes of Mononuclear and Dinuclear Arene Complexes, M = Fe, Ru", Organometallics, 1989, 8, 1580.

IV. Participating Scientific Personnel

Principal Investigator: Russell N. Grimes, Professor of Chemistry

Postdoctoral Associates:

Joseph Lomax
James Davis, Jr.
Martin Attwood

Graduate Students (degrees earned):

Henry Boyter (Ph.D. August 1987)
Kathleen Kahler Fonda (M.S. May 1988)
Kevin Chase
Mark Benvenuto